

RECENT PROGRESS IN NON-PRECIOUS METAL CATALYSTS FOR PEM FUEL CELL APPLICATIONS

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The development of non-precious metal catalysts (NPMCs) that are practical for use at the cathode of polymer electrolyte membrane fuel cells (PEMFCs) would provide immense economic advantages, perpetuating the looming widespread commercialisation of these devices. NPMC materials with excellent activity towards the oxygen reduction, coupled with PEMFC performance approaching that of state-of-the-art platinum catalysts brings this technology one step closer to practical application. Currently, the stability of these materials is still limited, and developing NPMC with excellent activity, performance and operational stability is the holy grail of PEMFC catalyst research. Fundamental knowledge available, along with recent progress made in this field of research will be the subject of this review paper.

Keywords: fuel cell, energy conversion, electrocatalyst, oxygen reduction reaction, sustainable energy

INTRODUCTION

Polymer Electrolyte Membrane Fuel Cells

Steadily increasing environmental concerns and depleting fossil fuel reserves indicate that a global shift from internal combustion engine technologies to more sustainable alternatives, especially in the transportation and automotive sector, is required in order to ensure the wellbeing of future generations. Polymer electrolyte membrane fuel cells (PEMFCs) are considered a viable alternative, operating cleanly and efficiently off a steady supply of hydrogen and oxygen. For transportation applications specifically, PEMFCs have been touted as the most promising long-term replacement to the internal combustion engine, primarily due to their excellent energy storage densities offering long range accommodation, rapid start-up and refuelling times and dynamic power outputs in order to meet the transient demands encountered during driving conditions. Fuel cells operate off a continuous supply of hydrogen at the anode, which is reduced according to the hydrogen oxidation reaction (HOR) provided in Equation (1):



Simultaneously, oxygen (either pure or from air) is fed to the cathode, where it reacts with protons transported through the proton exchange membrane and electrons directed through the external circuit according to the oxygen reduction reaction (ORR) provided in Equation (2):



The overall reaction of PEMFC systems is provided in Equation (3):



whereby PEMFCs can provide efficient electrochemical energy conversion with only environmentally benign water emissions at the point of operation. Furthermore, with the potential to produce

hydrogen from renewable sources, PEMFCs are very attractive for a variety of modern applications. Despite significant advances realised over the past 20 years, with Canada home to many world renowned companies and playing a leading role in PEMFC research and development efforts; at the current state of PEMFC technology, widespread commercialisation of these devices is still hindered by several factors including their high cost and limited operational stability.

PEMFC Technical Targets and Challenges

For transportation applications, in order for PEMFC systems to gain commercial success amongst traditional internal combustion engine technologies, they must be comparable from both a cost and durability standpoint. In order to address these issues, the United States Department of Energy (DOE) has set several technical targets that must be met by 2015, most notably including cost reductions to \$30/kW, along with 5000 h of demonstrated operational stability (equivalent to 150 000 miles) whereby less than 10% of the performance is lost.^[1] Significant advancements over recent years has driven the cost of these systems down to \$49/kW, and improved the stability to 2500 h of operation; however the current system configurations and component materials may not be suitable to bridge the remaining gap between the current technological status and proposed technical targets.

At the root of several cost and durability issues facing successful PEMFC commercialisation efforts lies the electrocatalyst materials required to facilitate the inherently sluggish HOR and ORR at practical rates for PEMFC performance. Currently, the electrocatalyst material of choice is platinum nanoparticles monodispersed on a high surface area carbon support (Pt/C). Notably, the

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ORR kinetics are five orders of magnitude slower than the HOR kinetics, resulting in significantly higher platinum requirements and loadings at the cathode which is the primary source of efficiency losses during PEMFC operation. Unfortunately, the excessive and steadily increasing cost of platinum provides a significant economic burden to the manufacture of PEMFC systems. As a precious metal commodity, the economy of scale will have no impact on the raw cost of platinum based catalyst materials and James et al.^[2] predict that in 2015, using very low platinum cost estimates of 1100 per troy ounce that for the mass production of 500 000 PEMFC transportation units, the platinum based catalyst layers will comprise over 30% of the total stack cost. Moreover, the stability of Pt/C electrocatalyst materials cannot meet the 5000 h of operation 2015 technical target, owing to performance losses due to corrosion of the carbon support, along with platinum nanoparticle dissolution, agglomeration and/or poisoning.^[3] Therefore, the development of unique electrocatalyst technologies that reduce or eliminate the need for platinum materials is urgently required. These materials must be capable of simultaneously combining high ORR activity with excellent operational stability and can serve to effectively perpetuate PEMFC technology from the research and development stage to large-scale implementation.

Electrocatalyst Approaches

While strong efforts have been made to reduce the overall platinum requirement for PEMFC systems, in the long-term these advances may very well be offset by the increasing and highly volatile price of platinum metal. Therefore, it would be ideal to develop non-precious metal catalyst (NPMC) materials that can be utilised at the cathode of PEMFC systems. NPMC research and development efforts have involved several different approaches, including the development of transition metal oxides, nitrides and/or carbides,^[4–8] transition metal chalcogenides^[9–13] and conductive polymers.^[14–17] The most promising NPMCs to date however have been a class of pyrolysed transition metal–nitrogen–carbon complexes which will be the focus of the present review, and for review of the other available NPMC materials readers are referred elsewhere for detailed discussions.^[18–23]

The development of transition metal–nitrogen–carbon catalyst materials was first pioneered by Jasinski^[24] who demonstrated that macrocyclic cobalt phthalocyanine (CoPc) was capable of facilitating the ORR in alkaline conditions. Years later, Alt et al.^[25] expanded upon this study, demonstrating the potential of transition metal–N₄ chelates supported on carbon to facilitate the ORR in acidic solutions, albeit coupled with very limited stability. These stability limitations could be effectively overcome by a heat treatment of these transition metal–N₄ complexes under inert environments at temperatures in the range of 400–1000°C.^[26–28] These stability enhancements were furthermore accompanied by improved ORR activity of the pyrolysed NPMCs, indicating that high temperature heat treatments induce favourable structural and atomic reconfigurations that have been the subject of extensive investigation and debate in the scientific community. Another breakthrough was realised by Gupta et al.^[29] who demonstrated that NPMCs could be fabricated by the heat treatment of a simple mixture of carbon, nitrogen and transition metal sources. This provided significant economic advantages due to the relatively low cost of simple precursor materials in comparison with expensive macrocyclic complexes, along with providing a large degree of flexibility for NPMC research and development efforts.

NPMC Technical Targets and Challenges

With the inherently minimal cost of NPMCs in comparison with platinum based materials, using very high catalyst loadings at the cathode is an economically viable approach. By extension, the activity of the relatively much thicker NPMC catalyst layers (ca. 10 times thicker than Pt/C catalyst layers) are evaluated on a volumetric basis as opposed to a precious metal loading basis, whereby the DOE has set volumetric activity targets of 300 A cm⁻³ at a PEMFC voltage of 0.8 V (corrected for iR losses).^[1] Volumetric activity can be defined according to Figure 1 as a combination of the: (i) average active site turnover frequency (TOF), (ii) active site density and (iii) catalyst layer utilisation. For volumetric activity evaluation, cell voltages of 0.8 V or higher are used because at these potentials, PEMFC current densities are primarily dictated by the ORR activity of the NPMC, a product of the catalytic TOF and active site density. From a practical standpoint in terms of NPMC performance, these materials must be capable of achieving high power densities at lower cell voltages at which point catalyst layer utilisation becomes an important consideration.

TOF relates to the number of electrons that are transferred at a single ORR active site per second. Catalyst TOFs are directly related to the kinetics of the ORR occurring at defined operating conditions, and are furthermore active site structure dependent, directly influenced by the exact nature and surrounding environment of the ORR active moieties present in the catalyst materials. For NPMC materials, the average TOF takes into account all of the different active site structures that may be present in different forms and quantities, possessing different site specific TOFs. The NPMC active site density is a product of the concentration of active site structures per unit surface area, and the overall volumetric surface area of the catalyst materials. It is not dependent on the identity of the active site structure; however relies on the active site sizes, dispersion and overall catalyst morphologies. Dramatic improvements to NPMC TOFs and active site densities have been realised over recent years by deliberate selection and modification of the particular synthesis and treatment techniques utilised. This has resulted in significant performance enhancements that have perpetuated NPMC research and development efforts from a fundamental stage to its current status where it is considered extremely promising for practical PEMFC applications. These advances have resulted in a partial shift in focus from TOF and active site density improvements, to catalyst layer designs to improve mass transport and utilisation.

Finally, limited operational stability is the primary technical challenge facing NPMC deployment, owing to the harsh, oxidising

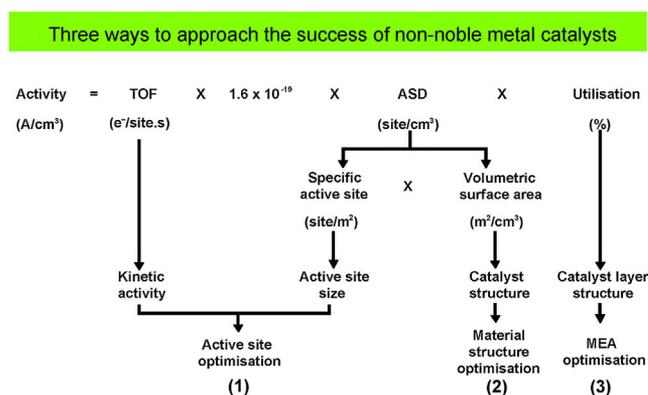


Figure 1. Practical approaches to improvements in NPMC performance, evaluated on a volumetric activity basis, from Ref.^[30]

conditions encountered at the cathode of PEMFCs during operation. The elevated temperatures, acidic environments and potentiodynamic conditions will induce NPMC degradation and debilitating performance losses long before the 5000 h stability technical target has been reached. While progress has been made towards understanding the specific degradation pathways, along with techniques to mitigate performance loss, limited NPMC stability is considered the primary barrier to successful adoption and commercialisation of this technology.

Scope of the Review Paper

The present review paper will focus on the significant advancements and research trends of NPMC research and development realised over the past 3–4 years, along with a discussion of potential strategies moving forward. Specifically, the review paper will be structured as follows. First, a discussion of non-pyrolysed transition metal–nitrogen–carbon complex catalysts will be provided. This is pertinent as this class of NPMC in the absence of high temperature heat treatments provides adequate structural control and certainty surrounding the exact identity of ORR active surface species. Therefore, investigations of these materials can offer important fundamental insight into this field of NPMC research and development, despite the fact that the practical application of non-pyrolysed NPMC may never be realised owing to the inherent performance and stability limitations. Following that, a thorough discussion of pyrolysed NPMCs will be provided with a particular focus placed on volumetric activity improvements. This discussion is deconvoluted into progress made toward improving: (i) ORR active site TOFs, (ii) catalyst active site densities and (iii) catalyst layer utilisation. Finally a discussion of NPMC stability will be provided, relating to the mechanistic pathways of NPMC degradation and proposed strategies to overcome this limitation.

NON-PYROLYSED NPMC

Early investigations of NPMC catalysts involved nitrogen coordinated transition metal macrocycle complexes supported on high surface area carbon based materials.^[25] Most commonly, cobalt- and iron-based macrocycles have been investigated, and have also been verified to provide the most promising ORR capabilities.^[31,32] Different transition metal macrocycle complexes have been investigated, including phtalocyanine and porphyrin structures, with a comprehensive review of the latter published recently to which the readers are referred for detailed discussion.^[33] As previously mentioned, despite the fact that the performance and stability of non-pyrolysed macrocycles may not be at the levels required for practical PEMFC application, adequate control and identification of the active site structures render investigation of these materials important from a fundamental perspective. Through these investigations, it has not only been exclusively demonstrated that the metal-ion centre type has a significant impact on the redox, and catalytic properties of these materials,^[34] but that the ligand structures and surrounding environment including macrocycle substituents and co-adsorbates have a large influence on catalyst performance.^[33,35]

Baker et al.^[36] investigated the activity of various substituted iron phtalocyanine (FePc) complexes adsorbed onto carbon support materials. The particular type of substituent group was found to have a strong impact on the adsorption properties of the FePc complexes, resulting in variations in the surface concentrations and configurations (i.e. flat, edge-on and agglomerate). Notably, significant differences in the ORR activity and stability of these complexes in acidic solutions were observed and could most

likely be attributed to the variations in surface arrangements as well as the modulated electronic properties of the metal-ion centre due to substituent group electronic effects.

Li et al.^[37] carried out an investigation on FePc based catalysts substituted with diphenylphthioether functional groups on the outer rings (Fe-SPC) as illustrated in Figure 2. With a structure inspired by that of naturally occurring oxygen activation catalysts, these materials were found to possess excellent ORR activity in acidic conditions. Moreover and most notably, a majority of the ORR activity of Fe-SPC was retained after immersion in acidic electrolyte and exposure to repeated electrode potential cycles. Conversely, FePc retained minimal activity after identical cycling procedures, consistent with traditional investigations of non-pyrolysed macrocycle complexes. The authors attributed the dramatic enhancements in stability to two primary factors. First, the electron donating behaviour of the functional thioether groups which can effectively suppress the formation and release of partially reduced oxygen based byproducts and intermediates that can have a detrimental impact on catalyst stability by deactivating neighbouring catalyst sites or the carbon support. Secondly, the bulky functional groups provide separation between the catalytically active centres, whereby the steric hindrance mitigates active site overlap and catalytic deactivation. Fundamental investigations of this nature exclusively illustrate the impact of structural modification on the electrochemical properties of transition metal macrocycles. By extension, the ORR activity and stability of these materials can be modulated, providing indication that by careful design and selection of macrocycle complexes, along with deliberate control of the surrounding environments, there is room for future progress and fundamental understanding of this class of catalyst. Knowledge gained from investigations of non-pyrolysed NPMCs can furthermore be applied in the case of pyrolysed catalyst design and synthesis as will be discussed in the

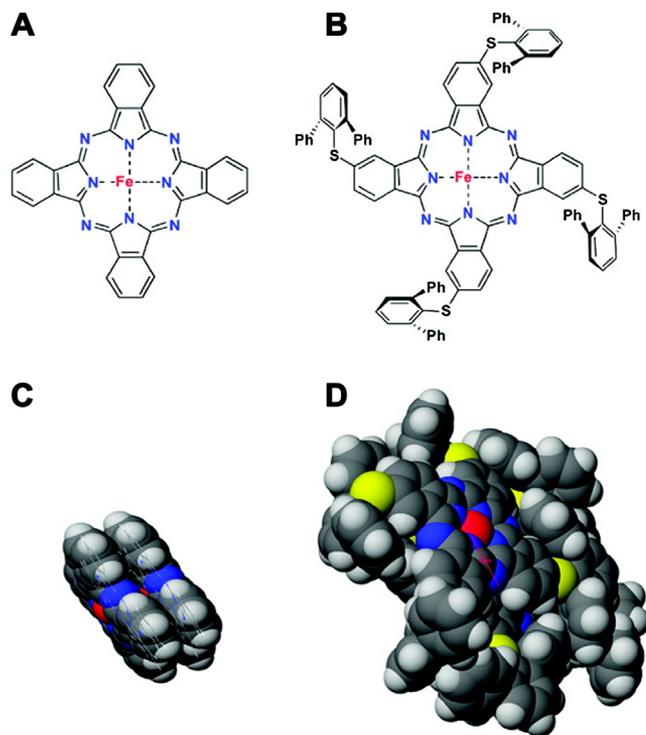


Figure 2. Atomic structure of (A) FePc, (B) Fe-SPC and space filling stack models of (C) FePc and (D) Fe-SPC. Reprinted with permission from Ref.^[37] Copyright 2010 American Chemical Society.

following sections, owing to the fundamental similarities between these two classes of materials.

PYROLYSED NPMC VOLUMETRIC ACTIVITY

With the performance of NPMC evaluated on a volumetric activity basis ($A \text{ cm}^{-3}$), variations in performance of different catalyst materials under identical operating conditions can be attributed to differences in the TOFs, catalyst active site densities or catalyst layer utilisation. Progress and fundamental understanding has been gained towards each of these considerations that will be discussed separately in the proceeding sections in order to provide a systematic summary of the factors governing NPMC volumetric activity.

Active Site Turnover Frequencies

The average TOF of NPMCs is directly dependent on the specific active site structures and geometries, as well as their respective concentrations. For this reason, it is highly pertinent to provide a discussion of the active site structures that have been proposed in the literature, a subject of ongoing debate. Following that, a discussion of the factors that influence active site TOFs will be provided. Although the specific active site structures and factors governing TOF vary depending on the specific precursor materials and fabrication techniques employed, some general trends have been suggested that can serve as a basis for future NPMC research and development efforts.

NPMC active site structure controversy

Owing to the elusive structural evolutions and morphological changes occurring during high temperature heat treatments of NPMC materials, coupled with limitations of existing structural and surface probing techniques, the exact identity and characterisation of the particular ORR active moieties present in this class of catalyst material has been the subject of controversy in the literature. Specifically, several researchers insist that the ORR active site structures are metal-ion centred,^[38–51] consisting of either Fe or Co species coordinated by nitrogen species in various configurations and entrained in the matrix of the carbon support materials. Conversely, other researchers claim that the ORR active sites consist of carbon–nitrogen functionalities,^[52–65] whereby the presence of transition metal species during NPMC synthesis is required only to catalyse the formation of these ORR active moieties. With a broad range of ORR active moieties proposed in the literature, it is highly likely that pyrolysed NPMCs contain a variety of different active site structures, governed by the specific synthesis techniques employed (i.e. precursor selection, heat treatment conditions and post-treatment procedures). It is furthermore highly likely that each of these active site species is present in different amounts, possessing varying degrees of ORR activity; culminating in the overall sample dependent differences in NPMC activity observed at identical potentials. Therefore, in order to fully understand the nature of NPMC activity, it would be beneficial to understand the impact of synthesis parameters on the identity and nature of active site structures, along with the resultant impact on catalyst TOFs in order to provide guidance for future research and development efforts.

Recent progress towards TOF improvements

Traditionally, the TOF of NPMCs was very low in comparison to platinum nanoparticle based catalysts, demonstrating an average of just 0.4 electrons being transferred per active site, assuming that each metal-ion participates as a single active site structure for the

ORR.^[66] In comparison, Pt/C catalysts possess average active site TOFs in the order of 25 electrons transferred per second, illustrating a significant gap between these two catalyst materials. In 2009 however, Lefevre et al.^[51] reported revolutionary results, whereby they reported NPMC materials prepared using 1,10-phenanthroline and iron acetate precursors and a two-step pyrolysis technique possessing turnover frequencies on par with Pt/C catalyst materials.^[66] This represented an over 40-fold improvement to the average active site TOF of NPMC materials, and for the first time making significant strides towards the practical application of NPMCs in PEMFC systems. The authors proposed that the active site structures in this catalyst consisted of micropore hosted Fe species, coordinated by nitrogen species present in two adjacent graphitic crystallites. Since that time, several reports have been published reporting high performance NPMC materials,^[67–70] supporting the prospect of NPMC deployment becoming a reality.

Factors governing active site TOFs

With some notable progress in NPMC activity already highlighted, it should be noted that the exact details surrounding the dramatic enhancement in active site TOFs remains unknown, and it would offer great insight for researchers to investigate and characterise this phenomenon further. Fundamentally speaking, it has been well established that the redox nature of the metal-ion centre in this class of active site structures will have a large impact on the electrochemical and catalytic properties^[34]; however how this can be translated and applied to pyrolysed NPMC development is still confounded.

On that note, Kramm et al.^[71] prepared various iron porphyrin based catalysts prepared using different heat treatment temperatures. The authors extensively characterised these materials by bulk elemental analysis, X-ray photoelectron spectroscopy and Mossbauer spectroscopy in order to gain insight into the impact of synthesis technique on the resultant catalyst properties and the variations in ORR activities. The primary conclusion drawn by these authors was that improvements in the ORR activity, and by extension the average TOF of the NPMC materials were due to increases in the electron density of the nitrogen coordinated metal-ion centres proposed to be the active site structures. Higher nitrogen contents in the carbon support materials were linked to increased electron densities of the Fe-ions, owing to the electron donor properties of these heteroatom dopants. Interestingly, this work can be related back to the fundamental investigations on non-pyrolysed NPMCs. Clearly, by modifying the ligand structure and surrounding environment of the ORR active sites (in this case by varying the thermal treatment temperature) it is possible to modulate the active site TOFs and resultant ORR activity of the catalysts.

Recently, the same authors in combination with the Dodelet group^[72] reported a detailed active site investigation using NPMCs prepared by high temperature ammonia treatment of carbon supports impregnated with varying amounts of iron acetate. Several different Fe-based species were observed in these catalyst materials using Mossbauer spectroscopy, with the highest activity attributed to Fe–N₄ species containing Fe²⁺ ions existing in a high spin state composite arrangement. Once again, the dramatic impact of the surrounding environment was elucidated in this study, whereby the proposed Fe-based active site structure possessing the highest TOF consisted of a 5th coordinating nitrogen species, along with the presence of a basic (protonable) nitrogen in close proximity (Figure 3A) that has a strong positive impact the active site TOF. The authors calculated the TOF of this active site configuration to be 11.6 electrons per second. This is lower than

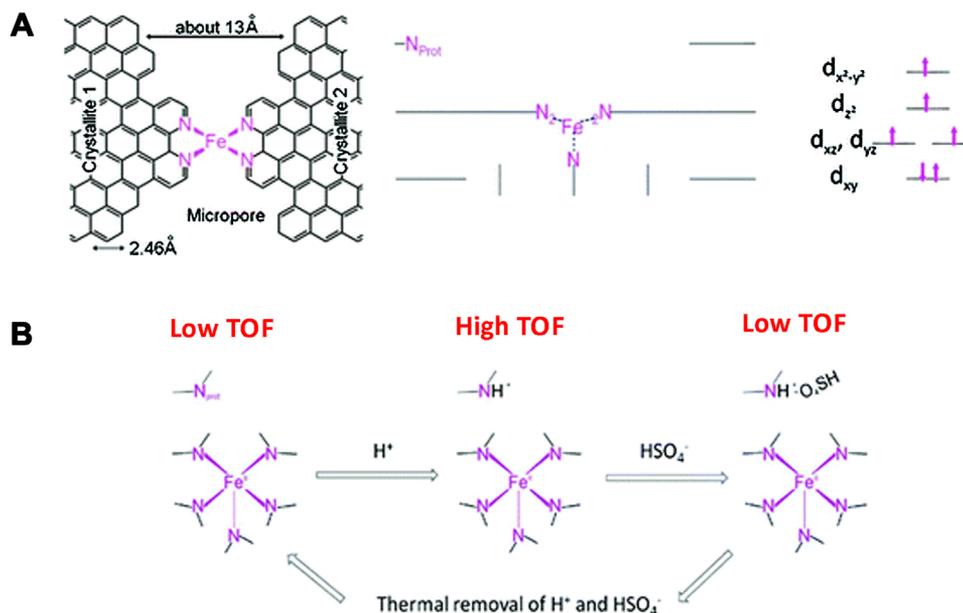


Figure 3. (A) Proposed active site structure with highest TOF (left) top view, (centre) side view and (right) energy scheme. (B) Various forms of the neighbouring basic nitrogen species in close proximity to the proposed metal-ion centred active site structure, including (left) low TOF unprotonated nitrogen, (centre) high TOF protonated nitrogen and (right) low TOF neutralised nitrogen. Reproduced from Ref.^[72] (adapted) with permission of the PCCP Owner Societies.

that reported previously for NPMC materials produced in the Dodelet group,^[66] most likely due to the different synthesis techniques used in each respective study and highlighting the fact that ORR activity is highly material dependent. Once again the dramatic influence of the active site surrounding environment was elucidated, whereby TOFs were highest when the neighbouring basic nitrogen species was protonated (Figure 3B, centre), and significant activity losses were observed if the protonated species was unprotonated (Figure 3B, left) or neutralised (Figure 3B, right).

Immense difficulty surrounds the adequate control and elucidation of the particular structural, electronic and compositional changes that occur during pyrolysis of NPMC materials. It has however been well established that the particular synthesis precursors, techniques and parameters utilised will have a significant impact on the resultant materials, particularly the identity of active site structure(s) and their respective TOFs. Drawing on recent progress in this field and an increased level of understanding, it should be a focus to develop effective NPMC fabrication techniques in order to deliberately control the selective formation of high TOF active surface species, with ideal structural geometries and coordinating environments.

Active Site Densities

The active site density refers to the number of available catalytically active sites per unit volume of NPMC, and is a product of the concentration of active site species per unit surface area, and the overall surface area of the catalyst particles. It is therefore ideal to obtain a monolayer of uniformly distributed active site structures covering the entirety of a high surface area carbon based support materials. Early NPMC development efforts utilised bulky macrocycle complexes which would tend to form agglomerates when adsorbed on the surface of carbon materials. A high temperature heat treatment could potentially alleviate the detrimental impact of active species agglomeration due to heat induced active site migration; however the carbonised products formed

during pyrolysis would result in pore blockages and inevitably low catalyst surface areas. It was thus considered a significant breakthrough in 1989 when Gupta et al.^[29] demonstrated the possibility of preparing NPMCs using simple organic and inorganic precursor materials instead of bulky macrocycle complexes. This provided enhanced capabilities and flexibility in the design and synthesis of unique NPMC materials. Primarily, using smaller precursor materials allowed researchers to utilise the entirety of the large surface areas of carbon support materials, to employ unique templated or self-supported catalyst approaches, or to utilise alternative support materials. All of these approaches offer potential to improve the active site densities of developed NPMC materials and will be discussed systematically in the following sections.

Synthesis approaches to increase active site densities

For over a decade Dodelet's group has carried out research on NPMCs fabricated by impregnation of carbon black support materials with iron salts, followed by high temperature (950°C) heat treatments in an ammonia environment.^[73-77] Based on their early work, they observed that for increasing heat treatment durations, increased catalyst weight losses were observed, with a maximum catalytic activity observed when the total weight loss was ca. 30-35 wt% range.^[78,79] Up to this point, the authors attributed the weight loss to micropore formation caused by ammonia induced etching of the disordered carbon phase present in the support materials, depicted schematically in Figure 4. Simultaneously, this etching would result in nitrogen incorporation into the graphitic crystallites, along with a reaction occurring between ammonia and the iron species resulting in the formation of catalytically active ORR sites hosted in the newly formed micropores.^[75] Longer heat treatment times would result in weight losses exceeding the optimal value, and were accompanied by losses in the ORR activity. The authors later verified the importance of high disordered carbon contents in the starting carbon support materials^[74] which allowed for the in situ

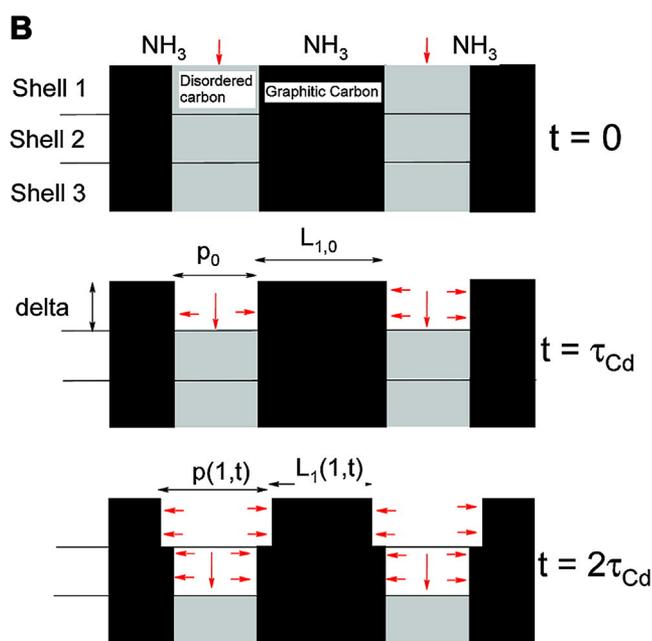
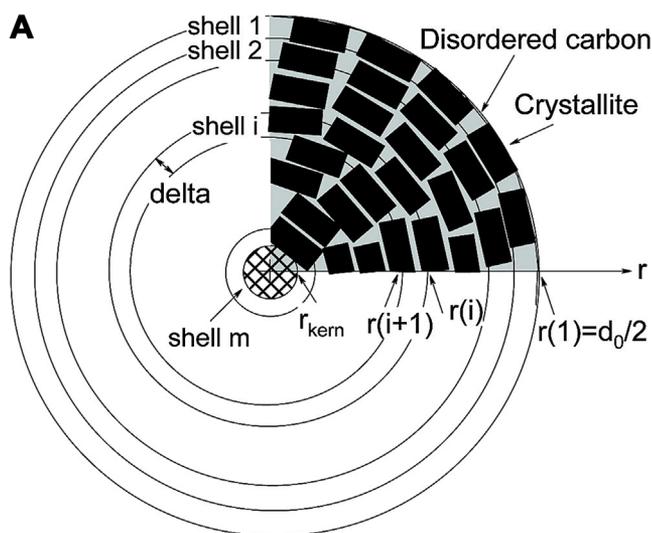


Figure 4. Schematic illustration (A) depicting the structure of carbon black containing disordered carbon (grey) and graphitic crystallites (black). (B) The preferential etching of disordered carbon by ammonia at a function of time resulting in micropore formation, whereby τ_{Cd} is the amount of time required to etch disordered carbon from a single shell of the carbon black. From Ref. [78] Copyright 2007 American Chemical Society.

formation of a larger number of micropore hosted active site structures. The author's proposed that the particular active sites formed in this class of catalyst had a FeN_{2+2}/C coordinated structure depicted in Figure 5, consisting of the Fe-ion bridging two adjacent nitrogen doped graphitic crystallites.

Recognising the importance of disordered carbon content and micropore formation during catalyst synthesis, Dodelet's group achieved a breakthrough in NPMC performance by adopting a unique impregnation and heat treatment strategy.^[51] Using a highly microporous Black Pearl 2000 carbon supports, the authors ballmilled these materials with iron acetate and organic 1,10-phenanthroline allowing impregnation and filling of the pre-existing micropores with these precursor materials. Upon an initial heat treatment in argon, carbonisation of the precursor materials

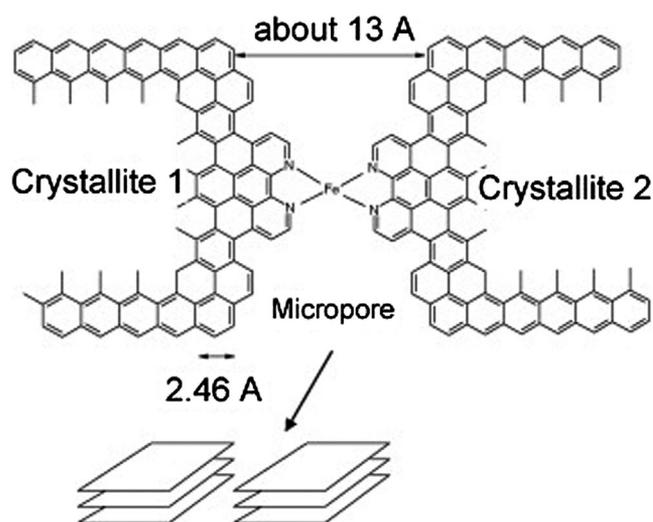


Figure 5. Schematic illustration of the proposed micropore hosted active site structures formed in situ during ammonia treatment of iron acetate impregnated carbon black. Proposed active site structure consists of a N_4 coordinated Fe-ion bridging two adjacent graphitic crystallites. Reprinted (adapted) from Ref. [48] Copyright (2008), with permission from Elsevier.

would occur forming the required disordered carbon phase deemed important for NPMC synthesis. Moreover, 1,10-phenanthroline is a nitrogen rich compound that could be an additional source of nitrogen doping, along with potential reaction with iron species forming catalytically active site structures entrapped in the disordered carbon phase. A second heat treatment under an ammonia environment was employed, resulting in etching of the newly formed disordered carbon phase, and formation/exposure of a high density of micropore hosted active site structures. Notably, the volumetric activity of these catalysts at an iR-corrected cell voltage of 0.8 V was 99 A cm^{-3} ; the highest NPMC catalyst reported at that time (2009), and approaching the previously established 2010 DOE target of 130 A cm^{-3} .

Zelenay's group employed a different approach for the synthesis of pyrolysed NPMCs, utilising transition metal salts in combination with nitrogen containing conductive polymers, more specifically polypyrrole (PPy)^[14,80] and polyaniline (PANI).^[68,81] Their preliminary investigations indicated that PANI based catalysts could provide superior ORR activity and improved stability^[80] and was the conductive polymer of choice for their breakthrough NPMC developments reported in 2011.^[68] In this work, the authors utilised Ketjen Black carbon supports mixed with aniline oligomers and transition metal salts (cobalt nitrate and/or iron chloride). Ammonium persulphate was then added to the mixture as a polymerisation agent, and the resulting FeCo-PANI/C composite was dried and subjected to a high temperature heat treatment in nitrogen. The catalyst materials were then subjected to acid washing in 0.5 M H_2SO_4 at $85^\circ C$ for 8 h, followed by a second pyrolysis in nitrogen in order to remove and surface inactive metallic species or residues. Through H_2-O_2 fuel cell testing, the catalyst containing a mixture of iron and cobalt was found to provide the best performance and stability, most notably a maximum power density of 0.55 W cm^{-2} at a cell voltage of 0.38 V (catalyst loading of ca. 4 mg cm^{-2}), and excellent performance retention after 700 h of potential hold at 0.4 V. The excellent performance of the FeCo-PANI/C based NPMC synthesised in this work can be attributed to a variety of factors. First, the authors claim that the structural similarities between aromatic PANI and

the graphitic support can lead to enhanced interactions and successful incorporation of nitrogen into the graphitic carbon structures following pyrolysis. Secondly, the high nitrogen content and polymeric structure of PANI ensures the uniform distribution of nitrogen species over the entire surface area of the carbon support. As nitrogen species have been deemed important for NPMC active site structure formation, the high nitrogen concentration, along with a uniform precursor surface coating and nitrogen distribution ensures that during heat treatment, excellent active site densities can be obtained on the NPMC surface. Finally, the acid leaching technique employed can effectively improve the overall active site densities due to the removal of inactive surface species that can block reactant access to underlying active site structures or pores. Carefully selecting catalyst precursor materials coupled with post treatment techniques to increase catalyst active site densities resulted in the development of one of the highest performing NPMCs to date, and holds significant promise for future NPMC research and development efforts.

Nitrogen-doped carbon nanotubes (N-CNTs) or nitrogen-doped graphene has been extensively investigated and characterised as effective ORR catalyst materials in alkaline conditions,^[82-95] or as platinum catalyst supports^[96-100]; however only limited investigations have highlighted their capabilities as NPMC materials for PEMFC applications.^[80,101,102] This is most likely due to the low density of active site structures on the planar walls of the N-CNTs capable of facilitating the ORR in acidic media. Particularly, previous research had highlighted the importance of large degrees of edge plane exposure for similarly structured materials to provide high active site densities and ORR activity.^[60,61] Recognising these limitations, Li et al.^[103] subjected commercial CNTs to an oxidative treatment in order to induce an abundance of defects and functional sites onto the formerly inert graphitic surface. These defects arose due to the partial unzipping of the outer CNT walls, forming nanoscale graphene sheets in large concentrations on the surface of the still intact CNT supports (Figure 6). These defect sites, in combination with residual iron species remaining from CNT synthesis were deemed important for the formation of a high density of active site structures during heat treatment in ammonia at 900 °C for 30 min. Using annular dark field scanning tunnelling electron microscopy, coupled with elemental mapping, the authors observed that the location of iron atoms was concentrated on the observed graphene sheets, present in close proximity with nitrogen species. This provides indication that these surface defect structures, generated in high concentrations by the surface oxidative treatment of CNTs could act as anchoring sites for the formation of ORR active surface moieties. Notably, an ORR on-set potential of 0.89 V versus RHE and half-wave potential of 0.76 V versus RHE were observed by electrochemical half-cell testing; however PEMFC performance evaluation was not provided and should be a subject of future interest.

Apart from harsh surface oxidising treatments, there are other techniques available in order to increase the edge plane exposure and active site density of NPMC materials. Choi et al.^[104] recently demonstrated the beneficial impact of simultaneously doping NPMC materials with nitrogen, phosphorus and boron. Fabrication was carried out by the high temperature (900 °C) pyrolysis of a mixture of the precursor materials and metal salts under an argon environment. The addition of phosphorus dopants into the fabricated NPMCs was demonstrated to provide marked ORR enhancements in comparison to NPMC materials doped with just nitrogen, or nitrogen and boron. Particularly, it was shown that phosphorus incorporation would disrupt the carbon lattice structures, resulting in a high concentration of edge plane exposure

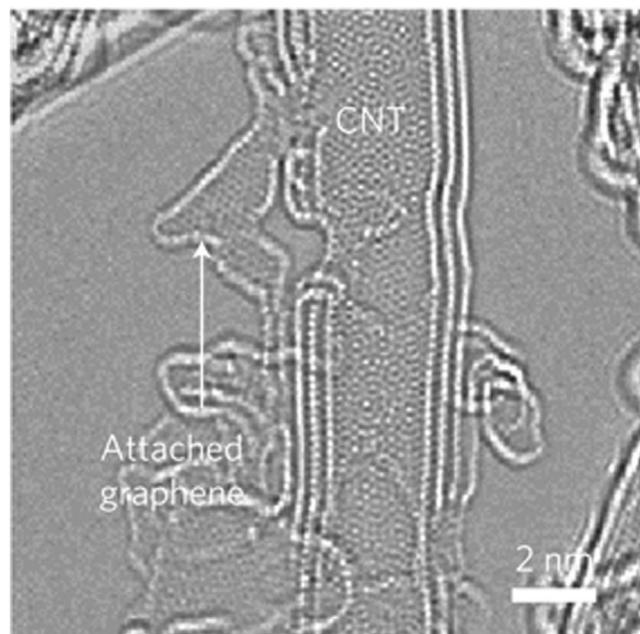


Figure 6. Aberration corrected TEM image of the NPMC materials fabricated by partial unzipping of the outer walls of commercial CNTs, followed by heat treatment in ammonia. The image demonstrates the successful formation of graphene defect structures on the surface of the CNTs that can serve as hosts for ORR active site structures. Reprinted with permission from Macmillan Publishers Ltd.: Nature Nanotechnology.^[103] Copyright 2012.

and wrinkled carbon morphologies. The increases in ORR activity were directly attributed to these morphology and surface structure modifications, highlighting the potential of introducing heteroatom dopants into NPMC materials in order to dramatically increase active site densities. Other dopant species, such as sulphur incorporation into NPMCs^[105,106] has also been investigated; however the exact impact on the resulting catalyst structure and ORR active site densities was not exclusively investigated. Further investigations into the impact of different dopant species (i.e. phosphorus, sulphur and boron) incorporated into NPMCs provides an interesting approach to increase active site densities and potentially beneficially modulate the electronic properties of developed materials.

Template strategies to prepare self-supported NPMC

When utilising carbon supports, it is possible to develop techniques as previously discussed in order to increase the active site densities on the surface and in the pores of the carbon particles. This allows for significant increases in the number of active sites per unit surface area of the NPMC; however, when applying similar techniques, only the outer surface area and some of the pore structures of the carbon support particles are capable of hosting active site formation, and furthermore the resulting overall catalyst surface areas are generally low following high temperature pyrolysis. In order to realise practical NPMC volumetric activity enhancements, it would be beneficial to develop catalyst materials with significantly higher overall surface areas, along with active site structures distributed throughout the bulk of the catalyst and not just on the surface of the carbon support materials. Sacrificial template strategies have been adopted in order to overcome this inherent limitation of using carbon support materials as the NPMC backbone.

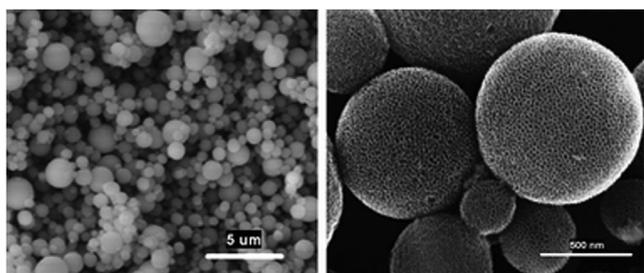


Figure 7. (Left) Ultrasonic spray pyrolysed Fe-PPy based catalysts impregnated inside silica templates. (Right) Mesoporous Fe-PPy catalysts after removal of silica template by etching in HF. Reprinted from Ref.,^[108] with permission from RSC.

Liu et al.^[107] reported an interesting ultrasonic spray pyrolysis technique to prepare cobalt and iron^[108] based NPMCs in the absence of any carbon support materials. The authors innovatively coupled ultrasonic spray pyrolysis with colloidal silica templating in order to produce Fe-PPy based spheres (Figure 7) that possess a highly mesoporous structure and exemplary surface areas of $1263 \text{ m}^2 \text{ g}^{-1}$.^[108] This surface area was over seven times higher than that of a similar NPMC fabricated using a conventional Vulcan carbon black support. The impact of high surface area and active site structures dispersed throughout the entirety of the catalyst particles was evidenced by the Fe-PPy mesoporous spheres obtaining a maximum power density of 62 mW cm^{-2} in an H_2 -air fuel cell; 3.4 times higher than that of the carbon black supported catalyst.

Serov et al. fabricated unique NPMCs using sacrificial silica support templates as schematically illustrated in Figure 8. The authors impregnated iron containing complexes and poly(ethyleneimine)^[109] or aminoantipyrine.^[110] High temperature heat treatments at variable temperatures (700 – 900°C) and subsequent silica removal by HF resulted in NPMCs with high active site densities, porosity and surface areas around $1000 \text{ m}^2 \text{ g}^{-1}$. The optimised materials were found to provide excellent ORR activity and promising stability capabilities investigated by half-cell electrochemical testing methods. Although PEMFC performance was not evaluated, these templating techniques are very promising in order to produce NPMC with high active site densities, dispersed both throughout the bulk and on the surface of the catalyst particles.^[55,108–113] Moreover, with careful design and selection of the sacrificial template materials, the structure of the NPMC can be deliberately tailored in order to optimise pore structures, sizes and distributions that can further improve active site densities and provide enhanced mass transport properties when incorporated into catalyst layers.

Alternative high surface area support materials

Apart from utilising template strategies to generate high surface area NPMCs, it is also possible to utilise unique carbon based supports such as graphene materials that possess exemplary surface areas and unique physicochemical properties.^[114] Graphene oxide is commonly used as a starting material and can furthermore enhance the active site density of these catalyst materials due to the high degree of defects that could potentially aid in facilitating the formation of catalytically active sites on both the edge planes and within the graphene sheet structures during high temperature pyrolysis treatments.^[115] Interestingly, several reports published recently have highlighted the beneficial impact of preparing graphene supported NPMCs demonstrating high ORR

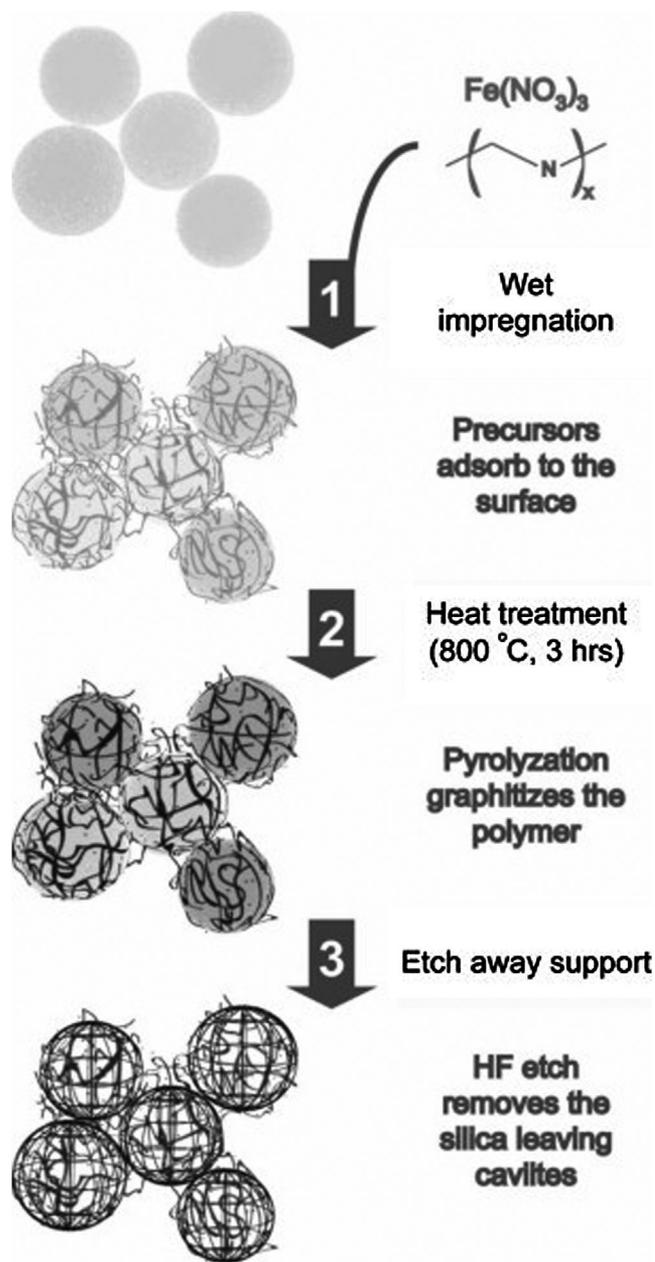


Figure 8. Schematic illustration of the silica templating approach involving (1) wet impregnation of silica template with iron and nitrogen containing precursors, (2) heat treatment in argon environment in order to carbonise NPMC materials and generate active site structure formation and (3) silica template removal by etching in HF. Reprinted from Ref.^[109] Copyright 2012, with permission from Elsevier.

activity and promising stability through half-cell electrochemical investigations.^[115–117] Notably, Choi et al.^[117] demonstrated improved ORR activity of NPMCs fabricated using graphene based supports in comparison to Ketjen Black 600JD carbon support. This indicates the promise of using unique, high surface area catalyst support materials to enhance ORR performance capabilities. While the direct impact of the high surface area and unique surface properties of graphene based supports was not exclusively elucidated, these results show the potential of graphene supported NPMCs with high active site densities, warranting further investigation and MEA testing.

Non-Precious Metal Catalyst Utilisation

With immense progress made recently, most notably in the past 2–3 years regarding NPMC catalytic TOFs and active site densities, a slight shift in focus towards catalyst utilisation has been observed in the literature. When dealing with significantly higher catalyst loadings, NPMC catalyst layers have thicknesses up to and exceeding $100\ \mu\text{m}$, at which point mass transport limitations present an issue facing PEMFC performance.^[118] Commonly, evaluating catalyst layer performance at a cell voltage of $0.6\ \text{V}$ is appropriate, providing a balance between cell efficiency and practical power output.^[70] At this cell voltage, the measure current densities and power output are influenced by a combination of the ORR activity of the NPMC (TOF and active site densities), along with catalyst layer utilisation. Despite significant advancements in NPMC activity, through MEA testing the best performing NPMC materials have previously only been capable of providing approximately one-quarter to one-third of the power densities obtainable by commercial Pt/C based catalyst layers.^[51,56,67–69]

Achieving high power densities at $0.6\ \text{V}$ and improved maximum power densities at lower potentials remains a pertinent technical challenge primarily due to poor reactant access and product removal throughout the entirety of these thick NPMC based catalyst layers. Previous investigations on Pt/C based catalyst layers have indicated the importance of meso and macroporosity in order to ensure adequate mass transport properties, along with the impact of ionomer content and distribution.^[119,120] Owing to the relatively recent emergence of NPMC materials that are approaching practical performance targets for PEMFC integration, studies of this nature are virtually non-existent. Despite the need for similar investigations in the near future, current researchers can apply the fundamental insight provided for Pt/C layers to deliberately design NPMC morphologies and catalyst layer structures to provide favourable mass transport properties.

Dodelet's group^[70] recognised that poor catalyst layer utilisation would limit the practical power densities of their developed NPMC materials and devised a strategy to combine their 1,10-phenanthroline/iron acetate impregnation technique with a template material. Recognising the previously established importance of NPMC microporosity on catalyst activity^[51,75] and the need for highly meso and macroporous electrode structures to improve catalyst utilisation, these researchers observed that they couple these two considerations by using a Zn(II) zeolitic imidazolate framework for catalyst synthesis.^[70] This metal-organic framework was first impregnated by the precursor materials by ballmilling, followed by two pyrolysis treatments first in argon (1050°C for 1 h) and then in ammonia (950°C for 15 min). The fabricated NPMCs demonstrated micropore and mesopore surface areas of 814 and $184\ \text{m}^2\ \text{g}^{-1}$, respectively. Notably, as illustrated in Figure 9, the best performing catalyst in this work provided a power density of $0.75\ \text{W}\ \text{cm}^{-2}$ at a cell voltage of $0.6\ \text{V}$, and a maximum power density of $0.91\ \text{W}\ \text{cm}^{-2}$, the highest reported performance for NPMCs to date. This performance (Figure 9, blue stars) was superior to catalyst materials prepared by a similar procedure, although using Black Pearls 2000 as a carbon support in place of the imidazolate template (Figure 9, red circles). Furthermore, the best performing NPMC had PEMFC performance approaching that of a state of the art Pt/C based catalyst layer with a loading of $0.3\ \text{mg}_{\text{Pt}}\ \text{cm}^{-2}$ (Figure 9, green squares). With a measured catalyst layer thickness of ca. $90\text{--}120\ \mu\text{m}$, the authors attributed the excellent performance to enhanced mass transport capabilities of the NPMC catalyst layer. Mass transport throughout the entirety of the catalyst layer was facilitated by the large mesopore content of the NPMC, consisting of

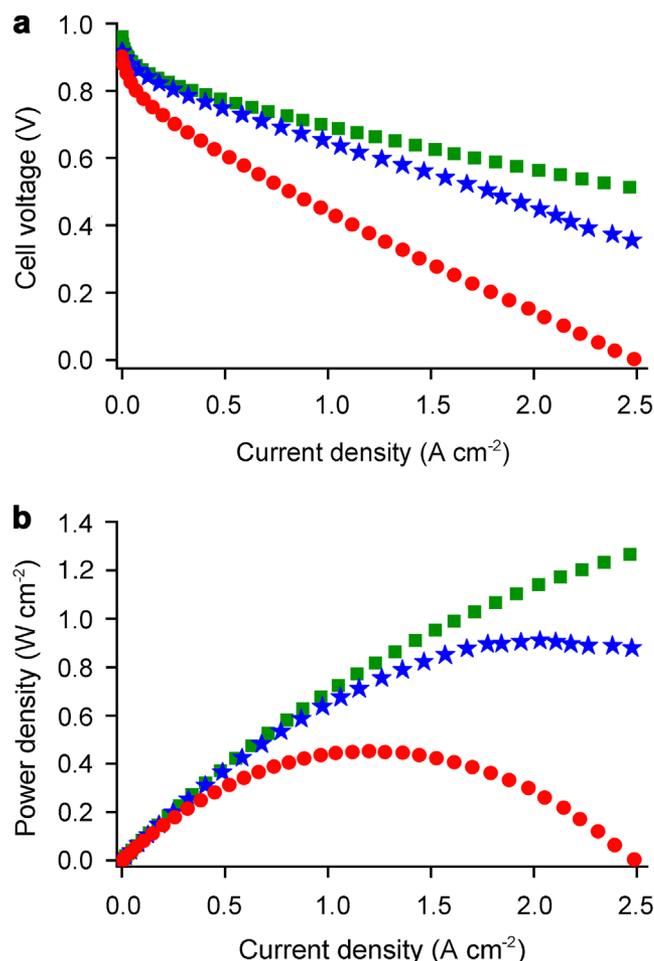


Figure 9. (A) Single $\text{H}_2\text{--O}_2$ cell polarisation and (B) power density curve of the best NPMC synthesised to date (blue stars), Ketjen Black supported NPMC (red circles) and commercial Pt/C (green squares) based catalyst layers. Reprinted by permission from Macmillan Publishers Ltd.: Nature Communications.^[70] Copyright 2012.

ca. $50\ \text{nm}$ diameter pores arranged in an alveolar-like interconnected structure observed by SEM imaging. Ideally, this NPMC reported the highest volumetric activity to date of $230\ \text{A}\ \text{cm}^{-3}$, effectively coupling excellent ORR activity and catalyst utilisation, and is well on track to meet the DOE target specification of $300\ \text{A}\ \text{cm}^{-3}$ by 2015.

Wu et al.^[69] devised an alternative technique to develop high performance NPMC materials with improved catalyst layer utilisation. These researchers initially pyrolysed a mixture of FePc and phenolic resin at 600°C , and then subjected it to acid washing in order to remove metallic iron species. Subsequently, they heat treated their materials at 800°C , and then again at 1000°C under an ammonia environment, with acid washing employed after each pyrolysis step. The beneficial impact of the second ammonia treatment at 1000°C (sample denoted 1000-III-NH₃) on MEA performance was most observable at higher current densities, whereby this NPMC did not demonstrate the mass transport losses that were characteristic of the other catalyst materials (Figure 10). These higher obtainable current densities were attributed to the formation of a highly porous structure due to ammonia etching at 1000°C , resulting in a mesopore surface area of $392\ \text{m}^2\ \text{g}^{-1}$. This was an approximately fourfold improvement in

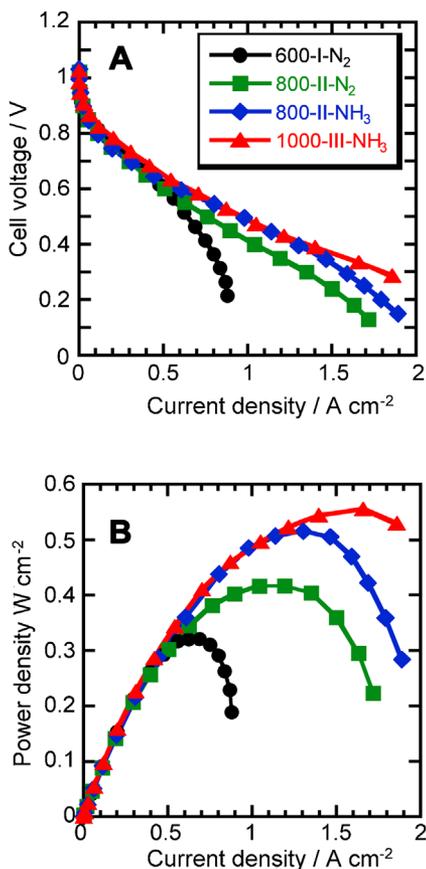


Figure 10. (A) Single $\text{H}_2\text{-O}_2$ cell polarisation and (B) power density curves. 600-I- N_2 is the catalyst precursors subjected to pyrolysis at 600°C in nitrogen which was the first step for the synthesis of all NPMC materials in this work. 800-II- N_2 was subjected to a second pyrolysis at 800°C in nitrogen, whereas 800-II- NH_3 was subjected to a second pyrolysis at 800°C in ammonia. The latter was then subjected to another pyrolysis at 1000°C in ammonia, resulting in the best performance 1000-III- NH_3 materials. Acid washing was employed after each pyrolysis step. Reprinted from Ref.,^[69] with permission from RSC.

mesopore surface area in comparison with the other materials prepared in this work.

Various alternative strategies exist to induce a high degree of mesoporosity into developed NPMC materials. As previously discussed, templating strategies, such as silica^[108–111] or soft-templating approaches^[65] can be utilised, or by employing metal oxalate precursor materials that can act as structure forming agents during catalyst synthesis.^[121] While scientists have the capability to deliberately control the morphology and pore structures of synthesised catalyst materials, there is a clear lack of understanding on the impact of NPMC pore sizes, structures and distributions, on practical PEMFC performance. Moreover, incorporation of ionomer into the catalyst layer will have a significant impact on the catalyst layer porosity, catalyst particle aggregate structures and mass transport properties of the catalyst layer.^[119,120,122,123] While these effects have been extensively investigated for Pt/C based catalyst layers, similar investigations are still required for NPMC materials. Results from combined computational and experimental studies will provide scientists specific guidance regarding the important factors governing mass transport and NPMC catalyst layer utilisation. Optimising these parameters will provide

opportunity to capitalise on the recent advances in NPMC activity in a practical manner.

NPMC STABILITY

At the current state of NPMC technology, the poor operation stability under PEMFC operating conditions is the primary factor limiting their practical application. Despite NPMC volumetric activity approaching the DOE technical target for 2015, the stability of these materials still falls significantly short of the stability technical target of 5000 h of operation with minimal ($<10\%$) performance loss. Several reports in the literature have indicated promising stability capabilities of newly developed NPMC materials; however these tests are generally carried by operating MEAs at low power or current densities. These testing protocols do not adequately simulate the practical conditions encountered during PEMFC operation, particularly the transient, potentiodynamic conditions required for transportation applications. It is thus of great interest to elucidate the exact sources of instability for NPMC materials, along with the particular mechanistic pathways of catalyst degradation in order to design techniques to mitigate or eliminate performance losses over long periods of operation.

Impact of Hydrogen Peroxide Species

The ORR can occur either by a four electron reduction mechanism, forming water, or by a less efficient two electron partial reduction mechanism, forming hydrogen peroxide species. Hydrogen peroxide is a highly oxidising molecule that upon release into the catalyst layer can be detrimental to the stability of the NPMC and other PEMFC component materials. It is therefore ideal to employ catalyst materials that preferentially reduce oxygen by the four electron reduction mechanism; however it is difficult to achieve 100% selectivity towards this reaction and some amounts of hydrogen peroxide species are unavoidable. To investigate the impact of hydrogen peroxide species on NPMC, researchers have treated catalyst materials in dilute solutions of hydrogen peroxide, whereby marked losses in ORR activity were observed.^[49,80] In particular, Lefevre and Dodelet^[49] immersed five different NPMCs in a 5 vol% solution of hydrogen peroxide for 5 h. The authors observed that all NPMC demonstrated a decrease in ORR performance after washing with DDI water and drying; however the magnitude of performance loss varied for each samples indicating that the impact of hydrogen peroxide species is material dependent, and no definitive mechanism of hydrogen peroxide induced degradation was determined. For a different set of NPMC materials, Koslowski et al.^[124] observed no ORR activity losses following 20 min of treatment in hydrogen peroxide, further confirming the material dependence of these treatments and indicating that the oxidative attack may be a slow process.

Impact of Ammonia Treatments

As previously discussed, some of the highest performance NPMCs are fabricated using high temperature heat treatments in ammonia. While ammonia treatment can provide high ORR activity, there is a clear trade-off in terms of stability. Meng et al.^[45] prepared a series of catalysts by pyrolysis treatments using different volume fractions of ammonia in the pyrolysis gas mixture. They observed that using even small amounts of ammonia (1.3 vol% in argon) would result in significantly improved ORR activity of the developed NPMC materials; albeit accompanied by a clear loss in stability. The authors linked this loss of stability to lower degrees of graphitisation in the catalyst materials in comparison with NPMC materials pyrolysed in pure argon. In a related study by Wu

et al.^[69] discussed previously, these authors observed excellent stability for materials pyrolysed in ammonia at 1000°C. The authors attributed this stability to the increased degree of graphitisation incurred at this high temperature despite the presence of ammonia, although no conclusive characterisations of the graphitic content were provided. The authors also ensured removal of surface iron nanoparticle species before ammonia treatment which may have a confounding effect on the stability of the NPMC materials (discussed in the next section).

Importance of NPMC Graphitisation

With carbon being the primary constituent element in NPMC materials, the importance of increased degrees of graphitisation on catalyst stability is a recurring trend.^[47,80] These stability improvements can be linked to two different factors. First, graphitic carbon has higher electrochemical stability and increased resistance to corrosion that may occur during PEMFC operation. Second, graphitic carbon contains less hydrophilic defect site structures that lead to water management issues and flooding of catalytically active site structures over long periods of operation that inevitably restrict reactant access and catalyst utilisation. In order to prepare highly graphitic NPMCs, several authors have proposed interesting techniques that will be discussed herein.

Based on their extensive work on conductive polymer based NPMCs, Zelenay's group reported that by using aromatic PANI precursor, an increased degree of graphitisation in their catalysts could be achieved, effectively resulting in increased resistance to degradation and improved electronic conductivity throughout the catalyst particles.^[68] Specifically, their most stable PANI based catalyst containing Co and Fe, was mixed with Nafion ionomer and subjected to a potential hold at a fuel cell voltage of 0.4 V. After 700 h of testing, the catalyst was found to maintain 97% of its current density. Interestingly, the mixed metal species catalyst had higher stability than the NPMC containing just iron, indicative of some sort of stabilisation impact of cobalt addition. The exact nature of this cobalt induced stability enhancement has not been conclusively determined; however has been reported elsewhere^[125,126] and may be linked to the cobalt catalysing the formation of more graphitic structures,^[125] or the ability of cobalt species to reduce hydrogen peroxide formation.^[127]

Exposing NPMC to heat treatments at higher temperatures will also result in increased levels of graphitisation. Commonly, by modifying the heat treatment temperature, a trade-off will be observed between ORR activity and stability. At increased temperature, increased graphitisation of the NPMC is accompanied by decomposition of a portion of the active site structures, resulting in higher stability but reduced performance, respectively. Recognising this trend, Wu et al.^[69] proposed that active site decomposition at elevated temperatures (>700°C) is enhanced by the presence of iron nanoparticles formed at lower temperatures during pyrolysis.^[128] In order to mitigate active site decomposition, the authors^[69] heat treated a mixture of FePc and phenolic resin at 600°C in nitrogen, followed by removal of iron particles by acid washing. Subsequently, heat treatments at higher temperatures (800 and 1000°C) in ammonia were employed, with ammonia acting as a source of nitrogen and etchant molecule to increase NPMC porosity. Figure 11 demonstrates results from H₂-air fuel cell stability investigations carried out by subjecting the MEA to a constant current density of 0.1 A cm⁻² and measuring changes in the cell potential. NPMC materials subjected to 800°C either in nitrogen or ammonia (800-II-N₂ and 800-II-NH₃, respectively) had significantly higher stability than the initial materials subjected only to heat treatment at 600°C in nitrogen. Furthermore, the

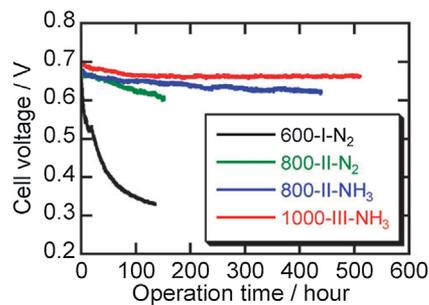


Figure 11. Single cell H₂-air voltage measurements maintaining a constant current density of 0.1 A cm⁻² for NPMCs. Reprinted from Ref.,^[69] with permission from RSC.

NPMC subjected to heat treatment at 1000°C in ammonia demonstrated the highest stability, retaining the majority of its cell voltage after 500 h of current density hold. The authors attributed the stability enhancements to higher degrees of graphitisation induced at higher temperatures; however no crystallographic characterisations were reported. This promising stability is contradictory to the previously established detrimental impact of ammonia species on NPMC stability. This suggests material dependence, or the necessity to remove iron particles and the exact nature of stability enhancements should be a focus of future investigations.

As an alternative to inducing graphitisation into NPMCs by high temperature heat treatments, it is also possible to use unique nanostructures and inherently highly graphitic carbon supports such as carbon nanotubes^[101,129,130] or grapheme.^[115-117] For example, Choi et al.^[117] prepared graphene supported NPMCs using iron acetate and pyrimidine-2,4,5,6-tetramine sulphuric acid hydrate as precursor materials. After heat treatment in nitrogen, the authors exposed the graphene supported NPMC to electrochemical half-cell accelerated degradation cycling testing. After 1000 potential cycles, the graphene supported catalysts demonstrated improved stability in comparison to commercial state-of-the-art Pt/C catalyst. Wu et al.^[80] demonstrated that preparing Fe-PANI based NPMCs using multiwalled carbon nanotube supports would result in higher performance and stability in comparison to catalysts prepared by an identical technique, albeit using Ketjen Black as the support. The benefits of using carbon supports with an inherently high graphitic content can allow researchers to circumvent the need to employ very high heat treatment temperatures, reducing the occurrence of active site deformation that occurs at these temperatures, while providing the necessary resistance to degradation and high electronic conductivity.

Proposed NPMC Degradation Mechanisms

Although there are some guidelines established in the literature with respect to NPMC stability, there is a clear lack of uncertainty surrounding the exact sources of NPMC performance loss. It is understandable that the NPMC type, including precursor materials and synthesis techniques employed, along with the surface properties including active site structures, functional species, defects and hydrophilicity/phobicity will all play an important role in NPMC; however the exact impact and influence of these factors remains unknown. It would be highly beneficial to elucidate the exact factors governing NPMC stability, along with elucidating the specific mechanistic pathways of catalyst deactivation. While results gained from studies of this nature may be material dependant, some general trends can be established that will

provide a fundamental understanding or NPMC stability in order for researchers to address this remaining technical challenge.

Popov's group^[56] synthesised a group of catalysts using FeCo-ethylenediamine chelate complexes impregnated in a silica template and subjected to pyrolysis at different temperatures and for different durations. This step was followed by silica removal, acid washing and re-pyrolysis. The impact of heat treatment time and temperature on ORR activity and stability was clearly demonstrated by these authors, and they utilised XPS before and after stability measurements (100 h of MEA potential hold at 0.4 V) to probe potential active site structures and degradation mechanisms occurring in this class of catalyst. Pyridinic and quaternary nitrogen species were proposed as the active site structure, and based on correlations between performance degradation and changes in the XPS spectra, the authors attributed the particular activity losses to protonation of pyridinic active site structures upon exposure to the acidic conditions encountered during PEMFC operation. This protonation as illustrated schematically in Figure 12 is facilitated by the lone pair of electrons characteristic of pyridinic nitrogen species, and inevitably results in deactivation of these catalytically active site structures.

Based on the ammonia heat treated catalysts extensively developed in the Dodelet group, these researcher previously reported an investigation pertaining to the specific degradation mechanisms occurring in this type of NPMC.^[131] The authors exposed their NPMC materials to acid washing in 0.1 M H₂SO₄ for 24 h, after which they observed marked performance losses. Interestingly, after a subsequent heat treatment in argon at temperatures as low as 300°C, significant recovery of the lost ORR activity was observed. The author's attributed the ORR activity loss to modification of a neighbouring nitrogen species in close proximity to the nitrogen coordinated iron-ion centre (the structure of which was depicted later by these authors and is displayed in Figure 3). Due to the basic nature of this neighbouring nitrogen species, protonation would occur upon immersion in acid, albeit not having a detrimental impact on the catalytic TOF. Subsequently, anion species could then bind to this protonated nitrogen species, resulting in a dramatic loss of the ORR activity, with the overall process depicted schematically in Figure 13. Interestingly, the protonation and anion binding step could be reversed by a heat treatment or chemical treatment with hydroxide, explaining the significant portion of ORR activity recovered by these procedures. Under the conditions employed in this investigation, specifically the utilisation of aqueous H₂SO₄, the rate of supply for anion species (HSO₄⁻) is very rapid. By extension, the rate of catalyst deactivation will be much faster in comparison to actual PEMFC operating environments where the

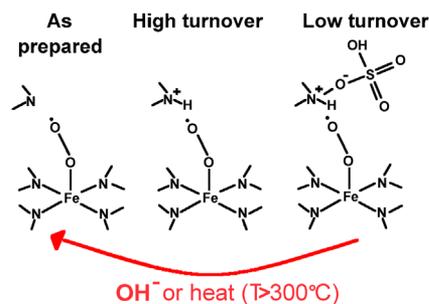


Figure 13. Schematic illustration of the active site structures present in NPMCs (left) as prepared, (centre) after immersion in acid and protonation, and (right) subsequent anion adsorption inevitably resulting in deactivation of the active site structure. Reprinted with permission from Ref.^[131] Copyright 2011 American Chemical Society.

rate of anion supply from the ionomer or polymeric membrane is much slower. An interesting link can be drawn between this study and the results discussed previously from Popov's group,^[56] both of which attribute NPMC activity losses to binding of ionic species to the basic nitrogen groups present in two different types of materials. Despite the differences in opinion between these two groups regarding the exact structure of the active site moieties and the identity of the ionic species deactivating the catalyst materials; the pertinent technical challenge is to establish techniques in order to prevent this occurrence of activity loss during PEMFC operation. Researchers should investigate structural and surface modifications, along with determining the impact of ionomer and membrane properties on the deactivation of the catalyst materials.

Practical NPMC Stability Validation

As previously discussed and highlighted throughout this section, at the current state of NPMC development and testing, stability investigations generally involve repeated electrochemical half-cell potential cycling, or operating single cell MEAs for continuous periods at low operating voltages or power densities. These utilised protocols can provide a gauge of catalyst stability capabilities; however do not simulate the actual conditions that will be encountered at the cathode during PEMFC operation, especially under the dynamic load conditions encountered for transportation applications. Furthermore, the impact of operating parameters including reactant feed type (air/oxygen), back pressures, humidity levels, temperature and stoichiometric ratios can impact catalyst stability, albeit with the magnitude of impact on NPMC stability unknown. With NPMC activity and performance levels approaching those practical for PEMFC applications, standardised degradation testing protocols must be developed specifically for NPMC in order to adequately investigate stability and catalyst deactivation. Furthermore, expanding on the work discussed herein, detailed diagnostic investigations directed at elucidating the specific degradation mechanisms occurring for NPMCs, along with appropriate design and development techniques to overcome these issues remains the primary technical challenges facing practical NPMC deployment.

CONCLUSIONS AND FUTURE OUTLOOK

With the potential economic benefits of successful NPMC development immense for the manufacture and marketability of PEMFC systems, significant research and development efforts have led to substantial progress in this field over recent years. The most promising catalyst materials in terms of performance and stability

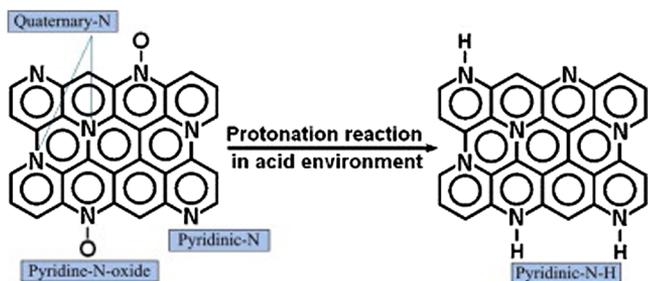


Figure 12. Schematic illustration of the proposed pyridinic species protonation that occurs under the conditions encountered at the PEMFC cathode deemed responsible for this activity losses in this class of NPMC. Reprinted from Ref.^[56] Copyright 2010, with permission from Elsevier.

are prepared by the pyrolysis of transition metal–nitrogen–carbon complexes. This class of NPMC comprised the scope of the present review.

To date, marked progress has been made towards meeting the NPMC volumetric activity targets set by the DOE for 2015 (300 A cm^{-3} at $0.8 \text{ V iR-corrected}^{[1]}$). Under these operating conditions, it is important to have NPMC materials with high ORR activity; a product of their TOF and active site densities. Several techniques have been developed in order to tailor and improve each of these properties that were discussed herein, and specific, standardised testing protocols should be developed that are broadly applicable and utilised in order to provide an accurate gauge of catalyst activity performance. Despite several recent reports of highly active NPMCs, there are a seemingly infinite number of precursor combinations, fabrication techniques and synthesis parameters that can be investigated. The exact impact of each parameter has confounded effects on the ORR activity; however several interesting trends and fundamental knowledge is now available that provides researchers ample opportunity to bridge the remaining gap between the highest volumetric activity NPMC synthesised to date (230 A cm^{-3})^[70] and the aforementioned 2015 DOE target.

In terms of practical PEMFC performance, NPMC materials must be capable of facilitating high current densities throughout the entire range of cell potentials encountered during PEMFC operation. To accomplish this, high catalyst layer utilisation is required, including effective mass transport throughout the entirety of the relatively thick ($100 \mu\text{m}$ or more) NPMC catalyst layers. By developing catalyst materials that effectively couple excellent ORR activity (TOF and active site densities), with high mesoporous surface areas, significantly improved NPMC performance could be obtained. Most notably, power densities obtained at a cell voltage of 0.6 V (a practical metric for PEMFC performance evaluation) for NPMC based cathodes have achieved ca. 75–90% of the capabilities of extensively developed and investigated Pt/C based cathodes.^[70] These excellent results are attributed to enhanced reactant access during PEMFC operation facilitated by the mesoporous structure of the catalyst materials. Due to the minimal cost of NPMC in comparison with platinum, this NPMC performance holds significant promise.

Now that there exists NPMC that can provide practical ORR activity and PEMFC performance, the most pertinent and proven difficult technical challenge is catalyst stability. To date, no materials have been able to effectively couple high performance and excellent operational durability. Some promising results have emerged over recent years, including a high performance iron–cobalt–polyaniline based NPMC that showed minimal activity degradation after 700 h of fuel cell potential hold at 0.4 V .^[68] While this holds some promise, the stability testing protocols most commonly employed do not adequately simulate the conditions encountered at the cathode during practical PEMFC operation, and moreover stability capabilities fall significantly short of the 2015 DOE technical target of 5000 h with minimal (<10% performance degradation). The exact effect of catalyst properties and operating conditions on NPMC stability still remains unknown; however ongoing investigations are focussed on elucidating these governing factors. Moreover, several recent studies have provided insight into the exact mechanistic pathway of NPMC performance loss. This fundamental knowledge will provide researchers enhanced capabilities in the future in order to design effective strategies in order to overcome these stability limitations.

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